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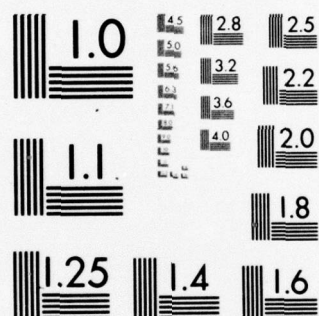
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by

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# THE GENERATION OF GEM-DIFLUOROALLYLLITHIUM

## BY THE TRANSMETALATION REACTION

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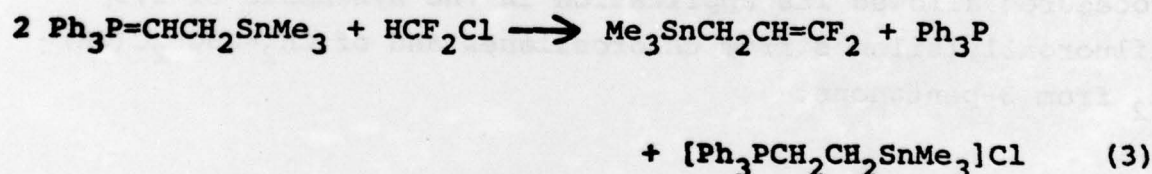
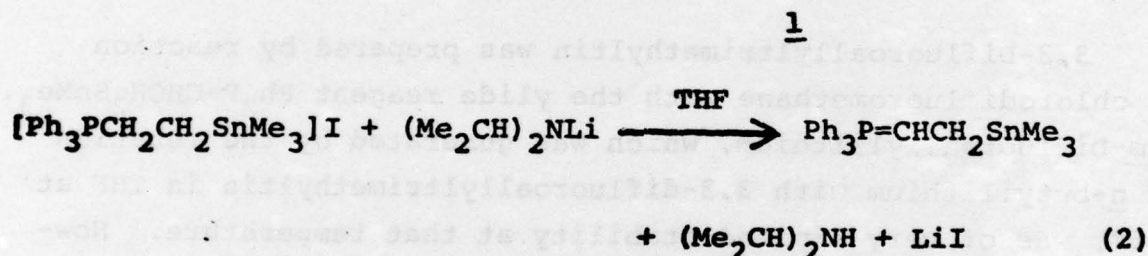
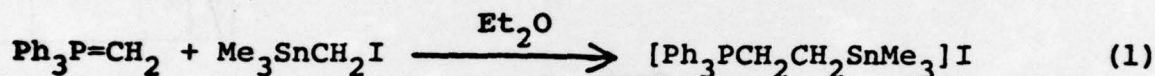
### Summary

3,3-Difluoroallyltrimethyltin was prepared by reaction of chlorodifluoromethane with the ylide reagent  $\text{Ph}_3\text{P}=\text{CHCH}_2\text{SnMe}_3$ . gem-Difluoroallyllithium, which was generated by the reaction of n-butyllithium with 3,3-difluoroallyltrimethyltin in THF at  $-95^\circ$ , was of very limited stability at that temperature. However, in situ procedures and alternate incremental addition procedures allowed its application in the synthesis of 1,1-difluoroallylsilanes from chlorosilanes and of  $\text{CH}_2=\text{CHCF}_2\text{C}(\text{OH})\text{Et}_2$  from 3-pentanone.

gem-Dichloroallyllithium, which can be prepared in good yield by the transmetalation reaction between  $\text{Ph}_3\text{PbCH}_2\text{CH}=\text{CCl}_2$  and n-butyllithium in THF and which is stable in THF below  $-80^\circ$ , is an ambident nucleophile which shows unusual regioselectivity in its reactions with carbonyl compounds (1). We have extended our studies of allyllithium chemistry to gem-difluoroallyllithium, a reagent, which, if accessible, would permit the synthesis of diverse unsaturated organofluorine compounds and whose regioselectivity in  $\text{C}=\text{O}$  addition would be of interest to examine.

An appropriate starting material of type  $\text{CF}_2=\text{CHCH}_2\text{Z}$  or  $\text{ZCF}_2\text{CH}=\text{CH}_2$  is required for the preparation of gem-difluoroallyllithium either by direct lithiation ( $\text{Z}=\text{H}$ ), ether cleavage with metallic lithium ( $\text{Z}=\text{PhO}$ ) or transmetalation ( $\text{Z}=\text{R}_3\text{Sn}$ ,  $\text{R}_3\text{Pb}$ ,  $\text{RHg}$ ). We have developed a procedure based on the latter reaction using  $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CF}_2$  as the difluoroallyl anion source.

The 3,3-difluoroallyltrimethyltin required for this study was prepared in good yield using a trimethyltin-substituted Wittig reagent (eq. 1-3). In the first reaction of this



sequence, ethereal triphenylphosphinemethylene is added to an ether solution of iodomethyltrimethyltin (2). The phosphonium halide which precipitates, 1, generally is contaminated with 10-15% of  $[\text{Ph}_3\text{PCH}_3]\text{I}$ . It can be purified by fractional crystallization to give analytically pure material, mp  $122.5\text{--}123.5^\circ$  (dec). However, for use in the eq. 2,3 sequence it need not be purified, as the  $\text{CH}_2=\text{CF}_2$  formed from the  $[\text{Ph}_3\text{PCH}_3]\text{I}$  impurity (via  $\text{Ph}_3\text{P}=\text{CH}_2$ ) is too volatile to interfere



in product isolation.

In the second step of this sequence the phosphonium salt is added to the cooled (ice bath) THF solution of lithium diisopropylamide\* in THF to give a cranberry-red ylide solution.

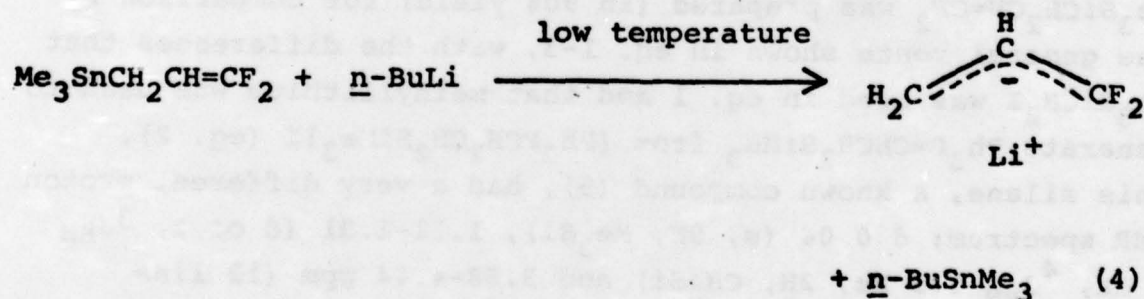
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\* Organolithium reagents, e.g., PhLi, cannot be used since they attack at tin as well as at the protons  $\alpha$  to phosphorus.

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Removal of the diisopropylamine formed in reaction 2 is essential in order to obtain good product yields in the subsequent step and to effect this, the volatiles are removed at 0.02 torr and 50° by trap-to-trap distillation into a receiver at -196°. The ylide which remains is redissolved in diethyl ether and treated, at 0°, with one-half molar equivalent of chlorodifluoromethane, following the procedure of Burton (3). The precipitated phosphonium salt is filtered and the filtrate is distilled. The product,  $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CF}_2$ , bp 129-131°,  $n^{25\text{D}}$  1.4465, is obtained in 74% yield and triphenylphosphine is recovered from the distillation residue in 79% yield.

Further experiments examined the preparation of gem-difluoroallyllithium from 3,3-difluoroallyltrimethyltin (eq. 4).



All experiments which were carried out to preform a solution of this reagent in this manner, prior to addition of the substrate, at temperatures between -95° and -130°, have failed thus far. The transmetalation does occur since n-



butyltrimethyltin is formed in good yield (73% in one such experiment which was carried out at  $-95^{\circ}$ , together with a 12% recovery of unconverted  $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CF}_2$ ). However, chlorosilanes can be converted to 1,1-difluoroallylsilanes in high yield by an in situ procedure in which n-butyllithium in hexane ( $\sim 2$  molar equivalents) is added slowly at  $-95^{\circ}$  to a mixture of  $\sim 1$  molar equivalent of  $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CF}_2$  and  $\sim 4$  molar equivalents of  $\text{R}_3\text{SiCl}$  in THF. Prepared in this manner were  $(\text{n-C}_3\text{H}_7)_3\text{SiCF}_2\text{CH}=\text{CH}_2$  (86%),  $\text{PhMe}_2\text{SiCF}_2\text{CH}=\text{CH}_2$  (75%) and  $\text{Me}_3\text{SiCF}_2\text{CH}=\text{CH}_2$  (64%) (yields by GLC after trap-to-trap distillation of the reaction mixture and concentration of the distillate).

It is of interest to note that the products had the structures shown, and not the isomeric  $\text{R}_3\text{SiCH}_2\text{CH}=\text{CF}_2$  structure. It would appear that as in the case of the gem-dichloroallyllithium-trimethylchlorosilane reaction, which gives  $\text{Me}_3\text{SiCCl}_2\text{CH}=\text{CH}_2$  exclusively (4), these reactions of gem-difluoroallyllithium are subject to kinetic control of product formation. The structure of the  $\text{R}_3\text{SiCF}_2\text{CH}=\text{CH}_2$  products was indicated clearly by their proton NMR spectra which showed only complex multiplets in the vinyl region ( $\sim 4.9$ - $6.4$  ppm), in addition to the resonances due to the R groups. In addition, the isomeric  $\text{Me}_3\text{SiCH}_2\text{CH}=\text{CF}_2$  was prepared (in 90% yield) for comparison by the general route shown in eq. 1-3, with the differences that  $\text{Me}_3\text{SiCH}_2\text{I}$  was used in eq. 1 and that methyllithium was used to generate  $\text{Ph}_3\text{P}=\text{CHCH}_2\text{SiMe}_3$  from  $[\text{Ph}_3\text{PCH}_2\text{CH}_2\text{SiMe}_3]\text{I}$  (eq. 2). This silane, a known compound (5), had a very different proton NMR spectrum:  $\delta$  0.04 (s, 9H,  $\text{Me}_3\text{Si}$ ), 1.11-1.31 (d of t,  $^3\text{J}_{\text{HH}}$  9 Hz,  $^4\text{J}_{\text{FH}}$  1.5 Hz, 2H,  $\text{CH}_2\text{Si}$ ) and 3.68-4.44 ppm (12 line pattern,  $^2\text{J}_{\text{HH}}$  9 Hz,  $^3\text{J}_{\text{FH(cis)}}$  3 Hz,  $^3\text{J}_{\text{FH(trans)}}$  24 Hz, 1H,  $=\text{CH}$ ) (in  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ).

The in situ procedure could not be applied successfully to the difluoroallylation of carbonyl compounds since the rate of attack of n-butyllithium at  $\text{C}=\text{O}$  appears to be greater than its rate of attack at tin. A successful addition of gem-

difluoroallyllithium to 3-pentanone, however, could be effected by a procedure in which a solution of  $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CF}_2$  ( $\sim 6$  mmol) in THF, cooled to  $-95^\circ$ , was treated alternately with 1 mmol portions each of *n*-butyllithium in hexane (over a 15 sec. period, with 30 sec. of stirring) and 3-pentanone (followed by 3 min. of stirring). This procedure of 1 mmol alternate additions was repeated identically at 3 min. intervals until 25 mmol of each reactant had been added. The product alcohol was isolated and characterized as its trimethylsilyl ether,  $\text{CH}_2=\text{CHCF}_2\text{Cet}_2\text{OSiMe}_3$ , and was obtained in 75% yield.

These experiments have demonstrated that gem-difluoroallyllithium, although it is of very limited stability at  $-95^\circ$ , can serve as a useful reagent, giving difluoroallyl group transfer in high yield, provided that appropriate procedures are used. Our further studies will examine its reactions with other substrates. Of special interest will be a study of its reactions with other carbonyl compounds. Its reaction with 3-pentanone parallels that of gem-dichloroallyllithium, which reacts with dialkyl ketones to give products of type  $\text{R}_2\text{C}(\text{OH})\text{CCl}_2\text{CH}=\text{CH}_2$  exclusively (1). It may be expected that gem-difluoroallyllithium will show similar regioselectivity, with the direction of addition to  $\text{C}=\text{O}$  being determined in the main by substrate electronic factors.

The availability of  $\text{Ph}_3\text{P}=\text{CHCH}_2\text{SnMe}_3$  and  $\text{Ph}_3\text{P}=\text{CHCH}_2\text{SiMe}_3$  provides a new and useful route for the synthesis of allylic tin and silicon compounds by Wittig reactions of our ylides with aldehydes and ketones. A separate report will detail our investigations in this area (6).

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